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Final Report:

Directionally Solidified Multifunctional Ceramics

Dr. A. Sayir

CASE WESTERN RESERVE UNIVERSITY

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Directionally Solidified Multifunctional Ceramics

I   INTRODUCTION

In order to achieve a significant increase in toughening and to retain the toughness at elevated temperatures a new multifunctional approach is proposed. The multifunctionality were achieved through directional solidification of polyphase materials comprising the load-bearing and functional phases. The functional phases include shape recovery and health monitoring. In parallel, new ideas about the load bearing phases were investigated to achieve tougher materials.

This projects addressed the two major challenges associated with structural ceramics. These challenges associated with ceramics are insufficient strength, low toughness and poor creep resistance at the very high temperatures of interest for aerospace applications. In order to achieve a significant increase in toughening and to further retain the toughness at elevated temperatures a new multifunctional approach was investigated. This final report summarize the findings toward the primary objective, which was to produce multiphase structures with superior mechanical properties (creep, high temperature strength and toughness) and formulate *in-situ* composite mechanics for multiphase structures. The research efforts on $Al_2O_3/RE_3Al_5O_{12}$ and $Al_2O_3/ZrO_2(RE_2O_3)$ with (RE = Y, Er, Gd, Nd, Ho, Eu) systems are summarized below, we expanded research on eutectics from the $Al_2O_3 - RE_3Al_5O_{12} - RE_2Al_2O_7$ (RE =rare earth oxides) and Al_2O_3 / Al_2MO_5 pseudobrookite (M = Ti, Fe, Mg) systems. We successfully accomplished to devise eutectic structures showing an acceptable level of toughness. Our recent finding revealed that the wear rate of a specific eutectic is four-orders of magnitude lower than current state-of-the art 'very good wear resistant' materials. Based on this finding, we propose additional study to elucidate wear resistance. The eutectic architecture of a continuous reinforcing phase within a higher volume phase or matrix, can be described as a naturally occurring *in-situ* composite. The mechanical properties of two phase eutectic are superior to that of either constituent alone due to the strong constraining effects provided by the coherent interfaces and microstructure [1-4]. The eutectics maintain a low energy interface resulting from directional solidification and can produce strong and stable reinforcing phase/matrix bonding [5]. The phases compromising a eutectic are thermodynamically compatible at higher homologous temperatures than man-made composites and as such offer the potential for superior high temperature properties [6].

The project also had an accompanying objective to research the multifunctionality. The multifunctionality comprises a plain combination of at least two functions or structure and function(s), smartness could be addressed as value-added multifunctionality. The multifunctionality was achieved wide range of applications be achieved through directional solidification of polyphase materials comprising the load-bearing and functional phase. Since the main tasks of load carrying and functionality (sensing and/or actuating etc) were investigated concurrently. However, we will only

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provide summary of some of our the major accomplishments for the load bearing application in this report (F49620-03-1-0128) and provide similar highlights for multifunctionality of specific systems.

II   EXECUTIVE SUMMARY OF SELECTED WORK

II.1.   Internal Stresses and the Creep Resistance of the Directionally Solidified Ceramic Eutectics

The creep resistance of the directionally solidified (DS) ceramic eutectic of Al_2O_3/c-$ZrO_2(Y_2O_3)$ was studied in the temperature range of 1200–1520 °C. The DS eutectic morphology consists of a topologically continuous majority phase of Al_2O_3, with a growth texture of [0 0 0 1] and an encapsulated minority c-$ZrO_2(Y_2O_3)$ phase in a variety of morphologies having a nearly <1 1 2 > texture. The two phases are separated by well-structured but incoherent interfaces. The creep of the eutectic in its growth direction exhibits an initial transient that is attributed to stress relaxation in the c-$ZrO2$ phase that also allows relaxation of large initial thermal misfit stresses between phases. In steady state creep, the DS eutectic shows many of the same characteristics of creep in sapphire single crystals with *c*-axis orientation. The creep strain rate of the eutectic has stress exponents in the range of 4.5–5.0 and a temperature dependence suggesting a rate mechanism governed by oxygen ion diffusion in the Al_2O_3. A finite element analysis of distribution of internal misfit stresses and those resulting from applied stresses in the two phases, together with a detailed dislocation model of the creep rate indicate that much of the nearly nano-scale encapsulated c-ZrO_2 is too small to deform by creep so that the major contribution to the recorded creep strain is derived from the diffusion-controlled climb of pyramidal edge dislocations in the Al_2O_3 phase. The evidence suggests that the climbing dislocations in Al_2O_3 must repeatedly circumvent the c-ZrO_2 domains acting like dispersoids resulting in the stress exponents larger than 3. The creep model is in good agreement with the experiments, and is generally supported by transmission electron microscopy (TEM) observations of dislocations in crept samples. Following conclusions are reached:

(1) In the eutectic of Al_2O_3/c-$ZrO2(Y_2O_3)$ the majority phase of Al_2O_3 is topologically continuous, has a nearly perfect texture of [0 0 0 1] parallel to the growth direction and encapsulates everywhere the minority c-ZrO_2 phase which itself has a growth texture of <1 1 2 >.

(2) The interfaces separating the phases are well-structured but are incoherent over most of the area.

(3) A large fraction of the c-ZrO_2 phase has a sub-micron oriented fibrillar or plate-like morphology which often, but not always, aggregates into colonies. The remaining fraction, usually surrounding the colonies of oriented fibrils or platelets is of a coarser, micron size.

(4) The eutectic morphology is stable against coarsening over periods of the order of 168 h at 1400 °C. The presence of a stress 300 MPa has also produced no measurable coarsening over the same length of time at 1400 °C.

(5) Upon first application of stress, transient creep is observed which is attributed to stress relaxation in the coarser fraction of the c-ZrO_2. The sub-micron fraction is considered to be too small to undergo deformation by crystal plasticity and is expected to be dormant.

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(6) In steady state creep stress changes do not produce additional transients within the resolution of stress measurements.

(7) The stress dependence of steady state creep rate is of power-law form with an exponent in the range between 4.5 and 5.0. The activation energy of the creep rate is 300 kJ/mol in the 1400–1500 °C range and is attributed to oxygen ion diffusion through the Al_2O_3 and along the interfaces.

(8) Because of the [0 0 0 1] texture of the Al_2O_3 phase which must control the overall creep rate for topological reasons, the proposed steady state model is based on the climb of the (1/3) [1 1 0 1] dislocations in Al_2O_3 since the latter are sessile in glide.

(9) In the creep model which is a generalization of the steady state diffusional creep model of Nabarro, the stress exponents of larger than 3 are attributed to the necessity of repeated bowing and straightening of the climbing dislocations in Al_2O_3 as they circumvent the sub-micron c-ZrO_2 domains.

(10) The predictions of the creep model, which has no adjustable constants, agree tolerably well with experimental observations.

(11) TEM observations were largely in support of the creep model and confirmed the presence of pyramidal dislocations in the crept samples.

(12) A few creep experiments on [0 0 0 1]-oriented sapphire crystals demonstrated a stress exponent of 3.5 at 1500 °C and showed creep rates very closely similar to those recorded in the eutectics.

II. 2. Creep Resistance of Directionally Solidified Ceramic Eutectics of Al_2O_3/C-ZrO_2 With Sub-Micron Columnar Morphologies

Directionally solidified laser float-zone-processed ceramic eutectics, having columnar morphologies made up of colonies of fibrilar and lamellar components of cubic ZrO_2 surrounded by a component of Al_2O_3 and having sub-micron morphological wave length, have a potential for remarkable creep resistance in the 1400 °C temperature range when stressed parallel to the growthdirection. The bulk creep response of both single crystalline Al_2O_3 and cubic ZrO_2 have been investigated extensively at this temperature and have shown no extraordinary promise for structural application. However, when directionally solidified and constituted in columnar eutectic morphologies with sub-micron wave length of phase dimensions, the restricted plasticity behavior that should occur can result in remarkable creep resistance. In many respects, this topology of constrained plasticity is expected to resemble that found in the CMSX-III super alloy single crystals.

While the present information on the morphology of the Al_2O_3 and c-ZrO_2 and the interaction of these components in the creep process of the directionally solidified eutectics is quite incomplete to reach many definitive mechanistic interpretations of behavior, some important conclusions can nevertheless be reached. The X-ray information on the registry of the topologically continuous Al_2O_3 lattice and the

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c-ZrO_2 lattice of the enclosed fibrils, the lamellae and coarser particles, as well as from fracture observations reported elsewhere, it can be concluded that interfaces between the two components are substantially incoherent even in the well ordered regions of the aligned fibrils and lamellae. Further, support for this observation comes from thermal residual stress measurements on eutectic systems similar to the present Al_2O_3/c-ZrO_2. Dickey et al. reported for the c-$ZrO2$-$NiO2$ system with similar directionally solidified morphology, having a coefficient of thermal expansion mismatch of $3.6\text{Å}\sim10^{-6}$ $°C^{-1}$, between components, in-plane residual stresses of the order of 1 GPa in the lamellar components at room temperature. In the present eutectic system of Al_2O_3/c-ZrO_2, this mismatch is larger at $4.0\text{Å}\sim10^{-6}\ °C^{-1}$, which with a similar difference between the solidification temperature and room temperature could result in similarly high residual tensile stresses in the c-ZrO_2 component at room temperature.

Since these high stresses do not relax readily, it must be concluded that interface slippage from fibril ends is of limited importance. Based on the above cited levels of residual stresses at room temperature it can be concluded that even at the test temperature of 1400°C there must be tensile residual stresses present in the c-$ZrO2$ of a magnitude close to 150 MPa, which is a substantial fraction of the applied tensile stress of 300 MPa in the experiments described above. Thus, at the start of the creep experiments, the tensile stresses in the c-$ZrO2$ fibrils and lamellae would be of the order of 450 MPa. Unlike in the CMSX-3 single crystal experiments of Pollock and Argon, where long incubation periods were found indicating an initial state starved of mobile dislocations, in the Al_2O3/c-ZrO_2 eutectic no incubation periods were found, suggesting that a sufficient initial population of dislocations is present in both components of the eutectic. We attribute the initially higher creep rate in the eutectic to be in a large part due to rapid stress relaxation in the c-$ZrO2$ component, which with a 111 axis orientation is well suited to undergo activate slip on the primary {100} 110 slip systems.

More importantly, from the measured overall relatively constant creep rate of $1.8\text{Å}\sim10{-5}\ s{-1}$ we must conclude that the topologically continuous majority Al_2O_3 component is also creeping over substantial portions of the rods at this temperature. Since after the primary creep phase of $4\text{Å}\sim10^{-3}$ strain, the c-ZrO_2 will have shed a significant fraction of its load support to the Al_2O_3 component, the stress in the latter could be considerably in excess of the 300 MPa level of the applied stress. Nevertheless, if the Al_2O_3 component had a coherent [0001] orientation throughout the rod, the high creep rates could not have been observed, or not be derived from glide on these planes. Thus, we must conclude that the periodic growth imperfections could either result in a significant fraction of the Al_2O_3 component to be misoriented away from the ideal [0001] axis orientation parallel to the rod axis, or that other pyramidal systems have been active. Clearly, a better accounting for the observed creep behavior will require a more accurate knowledge of both the morphology of the eutectic and deformation resistance of pyramidal systems in Al_2O_3.

In composites of the type of our eutectic, the rate controlling process must be that of the topologically continuous component, which in our case will be primarily basal slip in the Al_2O_3. This could be readily established from determination of the overall activation energy of the creep process. While on the whole the two components of the directionally solidified eutectic have a large measure of long range coherence, their interfaces are generally incoherent and there is no important crystallographic match between the basal glide system of the Al_2O_3 and that of the c-ZrO_2. Moreover, the Burgers vector magnitudes of the respective dislocations in the active slip systems are sufficiently different that slip in the two components must remain isolated across the interfaces. Therefore, apart from the need to maintain compatibility of deformation, the slip processes must develop independently

in the two components. This should give rise to channeling of the dislocations of the Al_2O_3 component among the c-ZrO_2 fibrils and lamellae, when such slip systems can be activated. A development resembling this behavior but in the c-ZrO_2 has been observed in ZrO_2, where the Y_2O_3 at 4.7 mol.% was insufficient to establish complete conversion to cubic form, these authors observed the formation of elongated lamellar precipitates of tetragonal ZrO_2. These then resulted in a well established dislocation channeling — type of flow in the intervening c-ZrO_2 components on a sub-micron scale with considerable elevation of the flow stress-resembling again the channeling behavior of slip in the components of the CMSX-3 superalloy crystals, reported by Pollock and Argon. Clearly, a variant of such enforced channeling will be an important source of the creep resistance of these eutectics. Many of these possibilities, which at present can only be conjectured, are currently under study and will be reported in the future.

II. 3.   High-Temperature Plastic Deformation of Er_2O_3-Doped ZrO_2 Single Crystals

The high-temperature plastic deformation of 5 mol% Er_2O_3-doped ZrO_2 monofilaments and rods processed by the laser-heated floating-zone method was studied using tensile and compression tests. The microstructure of the as-fabricated and plastically deformed crystals was characterized by scanning and transmission electron microscopy. The crystals were formed by a fine distribution of nano- meter-sized tetragonal variants with the c-axes mutually perpendicular, this particular microstructure being a consequence of the fast quenching associated with the fabrication process. A model is proposed to analyze the interaction between dislocations gliding in the multiple $\{1\ 0\ 0\}<0\ 1\ 1>$ slip planes and the interaction of dislocations with the tetragonal variants, taking into account the peculiar micro- structure of the material. The model explains the high work hardening observed in the system, the formation of unique plasticity-induced defects, and the high-temperature fracture mechanisms. These issues are discussed in comparison with previous studies of yttria-doped partially stabilized zirconia.

A model to explain the plastic deformation behavior of 5 mol% Er-PSZ single crystals fabricated using the laserheated floated-zone method is proposed. This model is based in the interaction between dislocations from the multiple $\{100\}<011>$ slip systems, and of these dislocations with the tetragonal phase. These interactions involve the formation of dislocation segments out of the slip planes, superdislocations with Burgers vectors close to the compression direction, and stacking faults associated with the precipitate shear. All these processes impede dislocation movement. The microstructure of these crystals, consisting of a fine distribution of three types of nanometer-size tetragonal variants originating from the fast cooling inherent to the fabrication process, does not allow mechanisms to release the stresses at the dislocation pileup front to be active. The model explains: The ''accelerated'' work hardening, not reported before for these systems. The formation of plasticity-induced defects, associated with the interaction of Lüders bands. The high-temperature fracture mechanism, in which cracks are generated by coalescence of such a defects.

II. 4.   High Temperature Creep Deformation of Directionally Solidified Al_2O_3/$Er_3Al_5O_{12}$

The microstructure of directionally solidified Al_2O_3/$Er_3Al_5O_{12}$ (19.5 mol% Er_2O_3) is analyzed and high temperature creep deformation studied using fibers in tension between 1400 ° C and 1550 °C. The directionally solidified Al_2O_3/$Er_3Al_5O_{12}$ system is an in situ composite and has a fine eutectic-

microstructure with sub-micron phase spacing. The microstructure is elongated in the direction of growth. Transmission electron microscopy observations revealed well-bonded interfaces and scatter within the crystallographic alignment of the constituent phases. The creep resistance of the system was very high, comparable to c-axis sapphire, and failure initiated at the lamella interfaces. The influence of the different elastic and plastic behaviors of the eutectic components on creep is examined. A critical discussion on the origin of the high stress dependence of the creep rate, the existence of steady state creep, and the relevant microscopic deformation mechanisms is presented.

The $Al_2O_3/Er_3Al_5O_{12}$ (19.5 mol% Er_2O_3) system grown by directional solidification produces a fine microstructure with a high density of well-bonded interfaces. This microstructure imposes an isostrain condition during elastic and plastic deformation. The different elastic and plastic properties of the two phases leads to a unique load transfer situation. There is load transfer to the garnet phase while this phase is deforming elastically that causes a continuous decrease of creep rate. During this transient regime the garnet phase deforms elastically and alumina deforms plastically. Following the initial region, both phases will be deforming at the same rate which is the global deformation rate of the $Al_2O_3/Er_3Al_5O_{12}$ eutectic. The lack of dislocations within the deformed specimens, the coarsening of the microstructure, the activation energies for creep, and the detailed study of the transient creep during loading and unloading conditions, leads to the conclusion that creep deformation of $Al_2O_3/Er_3Al_5O_{12}$ eutectic is diffusion controlled. Sliding at the interfaces does not accommodate diffusion and the system deforms in a non-steady

II. 5. Tensile Strength of Directionally Solidified Chromia - Doped Sapphire

Tensile fracture properties of directionally solidified chromia-doped c-axis sapphire fibers have been studied in a range of temperature (room temperature up to 1400 °C) and dopant content (0, 300 ppm and 1% of Cr2O3). Delayed failure of the fibers was studied by measuring the dependence of the tensile strength on the loading rate and by fractographic studies on the fracture surfaces of the fibers. In all the temperature range, the fibers doped with 300 ppm of Cr_2O_3 are slightly stronger than the pure sapphire fibers. The least strong fibers are those containing 1% of Cr_2O_3. For this badge of material, the beneficial effect of solution hardening is counterweighted by increasing amount of defects caused by a faster fabrication. Slow crack growth appears to be the process controlling delayed failure at higher temperature. Little contribution of slow crack growth to delayed failure is found at the lower temperature.

Directionally solidified pure sapphire and chromia-doped sapphire c-axis fibers, have been studied in tension from room temperature to high temperature under a range of stressing rates. Solution hardening is suggested to be responsible for the increase of tensile strength in the fibers with low dopant content, and internal defects are considered responsible of the reduction of tensile strength in the fibers with high dopant content. High-temperature static fatigue is found in all the fibers. Slowcrack growth is the dominant process to explain the dependence of the tensile strength on the stressing rate. Thermally activated bond rupture is suggested to be the microscopic mechanism controlling high temperature-stress crack growth in these sapphire-based fibers.

II. 6.   Stress Corrosion Cracking of Single-Crystal Tetragonal $ZrO_2(Er_2O_3)$

The flexure strength of partially-stabilized tetragonal $ZrO_2(Er_2O_3)$ single-crystal monofilaments manufactured by the laser-heated floating zone method was measured as a function of the environment (air versus water) and temperature (from 251 to 800 °C) at loading rates spanning three orders of magnitude to ascertain their susceptibility to the environmental conditions. These mechanical tests were completed with parallel tests on fully annealed monofilaments (to relieve the thermal residual stresses induced during growth) and by detailed analysis of the fracture surfaces using scanning electron microscopy and micro-Raman spectroscopy. While environmental susceptibility of $ZrO_2(Y_2O_3)$ in previous investigations was always associated with the destabilization of the tetragonal phase, monoclinic phase was not detected on the fracture surfaces of the $ZrO_2(Er_2O_3)$ monofilaments and it was concluded that slow crack growth in this material at high temperature or immersed in water was due to stress corrosion cracking.

The environmental susceptibility of partially-stabilized tetragonal $ZrO_2(Er_2O_3)$ single-crystal monofilaments manufactured by the laser-heated floating zone method was studied by means of three-point bending tests in air and water at 25 °C and in air from 25°C up to 800°C. It was found that the average flexure strength decreased markedly with temperature and it was lower in water than in air.Moreover, the flexure strength of the mono-filaments tested in water or above ambient temperature increased with the loading rate. This behavior was accompanied by significant changes in the morphology of the fracture surfaces. Those of the specimens tested in air at ambient temperature were rough, and brittle fracture was nucleated at a tiny surface defect. On the contrary, the fracture surfaces of the monofilaments tested at high temperature were smoother and showed an sample mirror region near the surface as a result of the slow crack growth of a crack upon loading. The mechanisms of slow crack growth in $ZrO_2(Er_2O_3)$ were different from those observed in tetragonal $ZrO_2(Y_2O_3)$. In particular, no traces of monoclinic ZrO_2 were found in the fracture surfaces of the $ZrO_2(Er_2O_3)$ which presented a severe drop in strength, while monoclinic ZrO_2 was always found in the fracture surface of $ZrO_2(Y_2O_3)$ which presented environmental susceptibility owing either to water or to high temperature. Annealing the residual stresses induced during processing did not modify the mechanical behavior of the $ZrO_2(Er_2O_3)$ monofilaments, and it is concluded the SCG in single-crystal $ZrO_2(Er_2O_3)$ at intermediate temperatures or immersed in water was due to of stress-corrosion cracking, as has been reported in single-crystal Al_2O_3.

II. 7.   High-Temperature Tensile Strength of Er_2O_3-Doped ZrO_2 Single Crystals

The deformation and fracture mechanisms in tension were studied in single-crystal Er_2O_3-doped ZrO_2 monofilaments processed by the laser-heated floating zone method. Tensile tests were carried out between 25°C and 1400°C at different loading rates and the dominant deformation and fracture mechanisms were determined from the shape of the stress–strain curves, the morphology of the fracture surfaces, and the evidence provided by monofilaments deformed at high temperature and broken at ambient temperature. The tensile strength presented a minimum at 600–800 °C and it was controlled by the slow growth of a crack from the surface. This mechanism was also dominant in some monofilaments tested at 1000 °C and above, while others showed extensive plastic deformation before fracture at these temperatures. The strength of plastically deformed monofilaments was significantly higher than those which failed by slow crack growth due to the marked strain hardening

capacity of this material.

The tensile deformation of single-crystal partially stabilized 5 mol% Er_2O_3-doped ZrO_2 was studied between 25°C and 1400°C. The tensile strength presented a minimum at 600 –800°C, which was associated with the slow growth of cracks from the surface. SCG was also present at 1000lC and above but it was not always the dominant fracture mechanism and some monofilaments tested in the range 1000l–1400°C presented higher ductility (13%–4%) as a result of the development of plastic deformation. They failed from process-related flaws at the surface and their strength was significantly higher than those that failed by slow crack growth due to the marked strain hardening capacity of this material.

II. 8.   Pulsed Laser Deposition of High Temperature Protonic Films

Pulsed laser deposition has been used to fabricate nanostructured $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ films. Protonic conduction of the fabricated $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ films was compared to the sintered $BaCe_{0.85}Y_{0.15}O_{3-\delta}$. Sintered samples and laser targets were prepared by sintering $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ powders derived by solid state synthesis. Films 1 to 8 μm thick were deposited by KrF excimer laser on porous Al_2O_3 substrates. Thin films were fabricated at deposition temperatures of 700 to 950 °C at O_2 pressures up to 200 mTorr using laser pulse energy densities of 1.4–3 J/cm^2. Fabricated films were characterized by X-ray diffraction, electron microscopy and electrical impedance spectroscopy. Single phase $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ films with a columnar growth morphology are observed with preferred crystal growth along the [100] or [001] direction. Results indicate [100] growth dependence upon laser pulse energy. Electrical conductivity of bulk samples produced by solid state sintering and thin film samples were measured over a temperature range of 100 to 900 °C. Electrical conduction behavior was dependent upon film deposition temperature. Maximum conductivity occurs at deposition temperature of 900 °C; the electrical conductivity exceeds the sintered specimen. All other deposited films exhibit a lower electrical conductivity than the sintered specimen. Activation energy for electrical conduction showed dependence upon deposition temperature, it varied from 115 to 54 kJ. Film microstructure was attributed to the difference in electrical conductivity of the $BaCe_{0.85}Y_{0.15}O_{3-\delta}$ films.

II. 9. Microstructure, Hydrogen Distribution and Electrical
Properties of Melt Grown High Temperature Protonic Conductors

A $Sr_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$ High Temperature Protonic Conductor has been produced using the melt growth process with the aim of reducing the grain-boundary blocking effect in proton conduction. The microstructure is characteristic of a cellular growth with cell dimension of 10–20 μm in width and 100 μm in length. The cells have distinct core and shell regions. A composition gradient in bivalent to pentavalent cation ratio is observed from the core to the shell. The cores act as channels for hydrogen diffusion. Nano-scaled domains have been revealed inside the cells identified as domains of 1:1 order of the cations on the B sites and orientation variants in the oxygen octahedra tilting. Ion Beam Analyses using a Nuclear Microprobe reveal only a slight hydrolysis of the surface after heat treatment of 10 h at 500 ∘C in wet air. Protonic conductivity is discussed and improvements are suggested by optimizing the calcium to niobium ratio of the constituent elements and designing larger cells.

A complex perovskite, $Sr_3(Ca_{1+x}Nb_{2-x})O_{9-\delta}$, has been produced by melt processing showing unique micro-structure that cannot be achieved by solid-state sintering. Melt processing provides an effective means to mitigate the issues of density, protonic transport rate and environmental durability of HTPC ceramics. Dense and elongated microstructures reduce the density of resistive boundaries perpendicular to the growth axis. Hydrolysis is confined at the first hundred nanometers under the surface as determined by Nuclear Micro-Analysis. The cell boundaries exhibit a better resistance to hydrolysis compared to sintered samples. Chemical gradients in the cells produce a core shell structure. A 1:1 ordered distribution of Ca^{2+} and Nb^{5+} following a random site structure is revealed by TEM and EDAX

II. 10. Wear Properties of Two-Phase Al_2O_3/ZrO_2 (Y_2O_3) Ceramics at Temperatures from 296 to 1073 K

Reciprocating sliding friction experiments were conducted with various two-phase, directionally solidified Al_2O_3/ZrO_2 (Y_2O_3) pins sliding on B4C flats in air at temperatures of 296, 873, and 1073 K under dry sliding conditions. Results indicate that all the Al_2O_3/ZrO_2 (Y_2O_3) ceramics, from highly Al_2O_3-rich to ZrO_2-rich, exceed the main wear criterion requirement of $10^{-6}mm^3N^{-1}K^{-1}m^{-1}$ or lower for effective wear-resistant applications. Particularly, the eutectics and Al_2O_3-rich ceramics showed superior wear properties. The composition and microstructure of Al_2O_3/ZrO_2 (Y_2O_3) ceramics played a dominant role in controlling the wear and friction properties. The controlling mechanism of the ceramic wear, friction, and hardness was an intrinsic effect involving the resistance to shear fracture of heterophase bonding and cohesive bonding and the interlocking microstructures at different scales in the ceramics.

The following comments are based on wear and friction studies conducted on two-phase, directionally solidified Al_2O_3/ZrO_2 (Y_2O_3) pins in contact with B_4C and other ceramics (SiC, Si_3N_4, and sapphire) in reciprocating motion at temperatures from 296 to 1073 K in air under dry sliding conditions. The main criterion for judging Al_2O_3/ZrO_2 (Y_2O_3) to be an effective wear-resistant material was the wear coefficient, which generally had to be on the order of $10K6$ mm^3 $N^{-1}m^{-1}$ or lower. In other words, wear resistance (the reciprocal of the dimensional wear coefficient) had to be on the order of 10^5 $mm^{-3}N^{-1}m^{-1}$ or greater. Although the wear coefficient of Al_2O_3/ZrO_2 (Y_2O_3) pins in contact with B4C flats increased as the temperature increased, all the two-phase, directionally solidified Al_2O_3/ZrO_2 (Y_2O_3) ceramics met this requirement at temperatures from 296 to 1073 K and are acceptable for effective wear-resistant applications. The eutectic ($65.07Al_2O_3/33.69ZrO_2$ ($1.24Y_2O_3$)—which had a Al_2O_3 to ZrO_2 ratio close to the eutectic composition) and $68.0Al_2O_3/30.8ZrO_2$ ($1.20Y_2O_3$) (Al_2O_3-rich ceramic with excess Al_2O_3) in contact with B4C surpassed the main wear criterion requirement and had a wear resistance 1–3 orders of magnitude higher than those of the highly Al2O3-rich ceramic ($72.6Al_2O_3/26.4ZrO_2$ ($1.00Y_2O_3$)) and the ZrO_2-rich ceramic ($62.7Al_2O_3/36.0ZrO_2$ ($1.30Y_2O_3$)). The two phase Al_2O_3/ZrO_2 (Y_2O_3) eutectic and Al_2O_3-rich ceramic showed strong and stable phase/matrix bonding during sliding in reciprocating motion. The interlocking microstructures at different scales contributed toward superior wear performance. The adhesive and abrasive interactions between Al_2O_3/ZrO_2 (Y_2O_3) and B_4C were both minimum for the Al_2O_3/ZrO_2(Y_2O_3) ceramics having the eutectic composition because the wear coefficients and coefficients of friction were at the minimum for the $65.07Al_2O_3/33.69ZrO_2$ ($1.24Y_2O_3$) eutectic. There was a correlation between wear coefficient and alumina concentration at each temperature. The correlation of the wear coefficient and alumina concentration consisted of two cases: the ZrO_2-rich ceramic, which had excess ZrO_2 and less Al_2O_3, and the Al_2O_3-rich ceramic, which had less ZrO_2 and excess Al_2O_3. The wear coefficient increased

with ceramics containing less ZrO_2 and more Al_2O_3 or containing more ZrO_2 and less Al_2O_3 than in the $65.07Al_2O_3/33.69ZrO_2$ $(1.24Y_2O_3)$ eutectic. The distortion, defects, and surface asperities caused by mechanical polishing tended to increase the wear coefficient. The coarse colony boundaries and pores of $Al_2O_3/ZrO_2(Y_2O_3)$ caused by the solidifying process also tended to increase the wear coefficient. The carbides B_4C and SiC can be effective counterpart materials for $Al_2O_3/ZrO_2(Y_2O_3)$ in a materials couple for wear resistant applications.

III   SUMMARY OF SCINTIFIC PUBLICATIONS

We summarize here the technical publications in peer reviewed journals, guest editing activities and list of invited talks and seminars. Forty two (42) referred journal publications have resulted from this work, as well as the twice the Guest Editing activity of Journal of European Ceramic Society. During the course of the project, we received additional funding through AFOSR project to investigate the multifunctional properties of the directionally solidified eutectic ceramics. Although the multifunctionality comprises a plain combination of at least two functions or structure and function(s), smartness, our focus always been on the primary functionality, which is load bearing characteristic. The scientific publications accomplished during the project entitled "Directionally Solidified Eutectic"(F49620-03-1-0128) included also the efforts on multifunctionality and hence the publications listed together. We published all of his papers in high quality research journals such as the Acta Materialia, Journal of American Ceramic Society, Solid State Ionics, Jounalof European Ceramic Society, Juournal of Materials Science, Tribology International, and numerous journals from different disciplines is a strong evidence of our national and international recognition. These papers that we authored and co-authored with our collaborators was a tremendous help to achieve high levels of complexity, significance and impact that are consistently accepted in the most demanding peer reviewed journals successfully.

IIIa.   SUMMARY PUBLICATIONS FOR DIRECTIONALLY SOLIDIFIED EUTECTICS

1. J-M. Fernandez, A. R. P. Gomez, J-J. Q. Cancapa, A. R. A. Lopez, J. LIorca, Y. Y. Pastor, S. C. Farmer and A. Sayir, *"High Temperature Plastic Deformation of Er₂O₃ – Doped ZrO₂ Single Crystals,"* Acta Materialia, 54 (2006) pp 2195 - 2204.

2. J. Y. Pastor, J. LIorca, P. Poza, J-J. Quispe, J-M. Fernandez, A. R. A. Lopez, A. Sayir, V. M. Orera, *"High Temperature Tensile Strength of Er₂O₃ – Doped ZrO₂ Single Crystals,"* Journal of the American Ceramic Society, 89 [7] (2006) pp 2140 - 2146.

3. F. Dynys and A. Sayir, *"Pulsed Laser Deposition of High Temperature Protonic Films,"* Solid State Ionics, 177 [26-32] (2006) pp 2333 - 2337.

4. M-H. Berger A. Sayir, F. Dynys, P. Berger, *"Microstructural and Electrical Characterisation of Melt Grown High Temperature Protonic Conductors,"* Solid State Ionics, 177 [26-32] (2006) pp 2339 - 2345.

5. P. Berger, J-P. Gallien, H. Khodja, L. Daudin, M-H. Berger and A. Sayir, *"Nuclear Microprobe Local Hydrogen Measurements in HTPC,"* Solid State Ionics, 177 [19-25] (2006) pp 1655 - 1658.

6. M-H Berger, A. Sayir and P. Berger, *"Microstructure, Hydrogen Distribution and Electrical Properties of Melt Grown High Temperature Protonic Conductors,"* International Journal of Hydrogen Energy, 31 [8] (2006) pp 1103 - 1111.

7. J. Ramirez-Rico, M. J. Lopez-Robledo, A. R. De Arellano-Lopez, J. Martinez-Fernandez and A. Sayir, *"Fabrication and Microstructure of Directionally Solidified $SrCe_{1-x}Y_xO_{3-\delta}$ (x = 0.1, 0.2) High Temperature Proton Conductors,"* Journal of European Ceramic Society, Vol. 26 [16] (2006) pp 3705 - 3710.

8. M. J. Lopez Robledo, J. Ramirez Rico, J. Martinez Fernadez, A. R. de Arellano Lopez and A. Sayir, *"Microestructura y comportamiento plastico de perovsquitas conductoras protonicas de alata temperatura"*. Boletin d la Sociedad Espanola de Ceramica y Vidrio, Vol. 44 [5] (2005) pp 347 – 352.

9. F. W. Dynys and A. Sayir, *"Self Assemble Silicide Architectures by Directional Solidification,"* Journal of the European Ceramic Society, Vol. 25 [8] (2005) pp 1293 – 1299.

10. J. Yi, A. S. Argon and A. Sayir, *"Creep Resistance of the Directionally Solidified Ceramic Eutectic of $Al_2O_3/ZrO_2(Y_2O_3)$: Experiments and Models,"* Journal of European ceramic Society, Vol. 25 [8] (2005) pp. 1201 -1214

11. A. Sayir, EDITORIAL, Journal of European Ceramic Society, Vol. 25 [8] (2005) pp v.

12. A. Ridruejo, J. Y. Pastor, Javier LLorca, A. Sayir and V. M. Orera, *"Stress Corrosion Cracking of Single-Crystal Tetragonal $ZrO_2(Er_2O_3)$,"* Journal of the American Ceramic Society. 88 [11] (2005) pp 3125 – 3130.

13. K. Miyoshi, S. C. Farmer and A. Sayir, *"Wear Properties of Two-Phase $Al_2O_3/ZrO_2(Y_2O_3)$ Ceramics at Temperatures from 296 to 1073 K,"* Tribology International, 38 [11-12] (2005) pp 1 - 13.

14. K. Miyoshi, K. W. Street, R. L. Vander Wal, R. Andrews and A. Sayir, *"Solid Lubrication by Multiwalled Carbon Nanotubes in Air and in Ultrahigh Vacuum,"* Tribology Letters, Vol.19 [3] (2005) pp 191 - 2001.

15. Y. B. Paderno, V. B. Filipov, V. N. Paderno and A. Sayir, "*Submicron Size Single Crystal Me(I)(V)B₂ (Me = Ti, Zr, Hf) Fibers,*" Journal of the European Ceramics Society., Vol. 25 [8] (2005) pp 1301 - 1305.

16. F. W. Dynys and A. Sayir, "*Self Assemble Silicide Architectures by Directional Solidification,*" Journal of the European Ceramics Society, Vol. 25 [8] (2005) pp 1293 - 1299.

17. J. J. Quispe-Cancapa, A. R. de Arellano-Lopez, J. Martinez-Fernandez and A. Sayir, "*Tensile Strength of Directionally Solidified Chromia-Doped Sapphire,*" Journal of the European Ceramics Society, Vol. 25 [8] (2005) pp 1259 - 1268.

18. C. Baudín, A. Sayir and M. H. Berger, "*Failure Mechanisms in Directionally Solidified Alumina-Titania Composites*", Key Engineering Materials, 290 (2005) pp 199 - 202.

19. A. Sayir, "*Carbon Fiber Reinforced Hafnium Carbide Composite,*" J. of Materials Science, 39 (2004) pp 5995 - 6003.

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22. H. Deng, E. C. Dickey, Y. Paderno, V. Paderno, V. Fillipov and A. Sayir, "*Crystallographic Characterization and Indentation Mechanical Properties of LaB₆-ZrB₂ Directionally Solidified Eutectics,*" J. of Materials Science, 39 [19] (2004) pp 5987 - 5994.

23. J. Yi, A. S. Argon and A. Sayir, "Creep Resistance of the Directionally Solidified Ceramic Eutectic of Al₂O₃ / c-ZrO₂(Y₂O₃)," Material Research Society, Vol. 791 (2004) pp 221 - 227.

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26. J. Martinez, M.-J. Lopez_Robledo, A. Ramirez-de-Arellano-Lopez, C. Real_Perez and A. Sayir, "Fabrication and Properties of High Temperature Proton Conducting Perovskites," The Electrochemical Society Transactions, 3 [1] (2006) 459 – 469.

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27. A. Sayir, S. C. Farmer F. Dynys, *"High Temperature Piezoelectric La$_2$Ti$_2$O$_7$,"* Ceramic Transactions, Advances in Electronic and Electrochemical Ceramics: Proceedings of the 107th Ann. Mtg. of the Am. Ceram. Soc., Vol. 179 (2006) pp. 57 – 69.

28. M. E.Brito, P. Filip, C. Lewinsohn, A. Sayir, M. Opeka and W. M. Mullins, Editors. Ceramic Engineering and Science Proceedings, *"Developments in advanced Ceramics and Composites.* A collection of papers presented at the 29th International Ceramics and Composites, Vol. 26 [8] (2005) 404p. and PREFACE, Vol. 26 [8] (2005) p ix.

29. F. Dynys and A. Sayir, *"Pulsed Laser Deposition of BaCe$_{0.85}$Y$_{0.15}$O$_{3-\delta}$ Films,"* Ceramic Engineering and Science Proc., Vol. 26 (2005) pp 57 – 63.

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33. K. Miyoshi, K. W. Street, R. L. Vander Wal, R. Andrews, D. Jacques, R. L. Vander Wal and A. Sayir, *"Solid Lubrication by Multiwalled Carbon Nanotubes in Air and in Vacuum for Space and Aeronautics Applications,"* Proc. of World Tribology Congress III – ASME (2005) pp 321 - 322.

34. J. D. Wrbanek, G.C. Fralick, S. C. Farmer, A. Sayir, C. A. Blaha, and J. M. Gonzalez, *"Development of Thin Film Ceramic Thermocouples For High Temperature Environments,"* AIAA 2004-3549, 40th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Fort Lauderdale, FL, July 2004.

35. J. D. Wrbanek, G.C. Fralick, S.C. Farmer, A. Sayir, C. A. Blaha, and J. M. Gonzalez, *"Development of Thin Film Ceramic Thermocouples For High Temperature Environments,"* NASA TM-2004-213211, Glenn Research Center, Cleveland, OH, August 2004.

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42. J. LLorca, A. Sayir, J. Y. Pastor. P. Poza, J. Quispe, A.R. Pinto, J. Martínez, *"Deformation and Fracture Mechanisms in $ZrO_2(Er_2O_3)$ Single Crystals,"* 27th Int. Conf. on Advanced Ceramics and Composites, (2003) pp 17 - 24.

IIIb. GUEST EDITOR:

1. Journal of European Ceramic Society, Vol xx, n. x, (2007) xx - xx.
"Directionally Solidified Eutectic Ceramics," .

2. Journal of European Ceramic Society, Vol. 25, n. 8, (2005) 1191 - 1462.
"Directionally Solidified Eutectic Ceramics," (2003).

3. Journal of Materials Science and Engineering, editorial board on the special issue on "Ultra High Temperature Ceramic Materials", (2004).

IIIc. INVITED PRESENTATIONS

1. A. Sayir, *"Proton Conducting Ceramics for 300 – 400 °C"* presented at the American Physical Society Meeting in Denver, CO, March 5-9, 2007.

2. A. Sayir, *"Piezoelectric Materials for Biological Actuation,"* presented Technion, ISRAEL, April 30, 2006.

3. A. Sayir, M-H. Berger, and S. C. Farmer, *"Melt Processed Mullite,"* presented in 2nd Int. Workshop on Mullite, Institute of Minerology and Crystallography University of Vienna, Vienna, AUSTRIA, June 11 -14, 2006.

4. A. Sayir, *"Melt Processing of Proton Conducting Ceramics for Hydrogen Separation,"* CIMTEC - 11th International Ceramic Congress and 4th Forum on New Materials, in Acireale, Sicily, ITALY, June 4 – 9, 2006.

5. A. Sayir, *"Hydrogen Separation Membrane Ceramics,"* Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, April 6, 2006. Urbana, IL.

6. A. Sayir, *"Piezoelectric Fibers Development for Energy Harvesting,". Los Alamos National Laboratory, December 12, 2005, Los Alamos, NM.*

7. J. Yi, A. S. Argon, and A. Sayir, *"Creep Resistance of the Directionally Solidified Ceramic Eutectic of Al_2O_3 / c-$ZrO_2(Y_2O_3)$ - Experiments and Models,"* 1st Directionally Solidified Eutectic Workshop in Paris, FRANCE, May 5th –7th, 2003.

8. A. Sayir, *"Characterization of HfO_2 - Ta_2O_5 System Using High Power Lasers,"* 29th Int. Conf. on Adv. Ceram. and Composites, Cocoa Beach, Fl, January 2005.

9. A. Sayir, *"Melt Processing of Structural and Functional Ceramics,"* presented at the 3rd Symposium of Energy and Environmental Science (3rd SEES) in YOTO Campus of Utsunomiya University, JAPAN, 2004.

10. A. Sayir, *"Multi-Functional Ceramics, Design Methodology for Melt Processing"* presented at the University of Akron, Akron, OH, 2004.

11. A. Sayir, *"Nano Scale to Macroscale Precipitation Effects Through Laser Processing of Ceramics"* 8th Europ. Ceram. Soc. Conf., June 29 – July 2, Istanbul, TURKEY 2003.

12. J. Martinez Fernandez, S. C. Farmer and A. Sayir, *"High Temperature Mechanical Behavior of Sapphire-Based Eutectics"* presented in the *Directionally Solidified Eutectic Ceramics Workshop, Paris, FRANCE, May 5 – 7, 2003.*